

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project (0455)

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE July 2001	3. REPORT TYPE AND DATES COVERED FINAL TECHNICAL REPORT 15 Nov 97 - 14 Nov 00	
4. TITLE AND SUBTITLE IN-SITU TOUGHENED A'-SIALON		5. FUNDING NUMBERS F49620-98-1-0126 2306/BX 61102F	
6. AUTHOR(S) I-WEI CHEN			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF PENNSYLVANIA PHILADELPHIA PA		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AIR FORCE OFFICE OF SCIENTIFIC RESEARCH 801 N. RANDOLPH STREET, ROOM 732 ARLINGTON, VA 22203-1977		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES <div style="text-align: right; font-size: 2em; font-weight: bold;">20010905 123</div>			
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE, DISTRIBUTION IS UNLIMITED		12b. DISTRIBUTION CODE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR) NOTICE OF TRANSMITTAL DTIC. THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLIC RELEASE LAW AFR 190-12 DISTRIBUTION IS UNLIMITED.	
13. ABSTRACT (Maximum 200 words) The grant was initiated on November 15, 1997. We have explored the compositions at which in-situ toughened a'-SiAlON can be obtained. This essentially encompasses the entire single a'-phase region. It includes both rare-earth ion-added compositions and alkali-earth ion-added compositions. We have made a systematic effort to obtain kinetic data on phase transformation at different compositions, since this knowledge is critically important for the precise control of nucleation and growth which dictate the microstructure. We have developed methods for controlling microstructure in a'-SiAlON prepared from commercial a-Si ₃ N ₄ powders. These materials have faster transformation rate and the microstructure control must rely on nucleation treatment of external seeding. We have developed the method to grow and harvest seed crystals, of a controlled composition, size and morphology, which can be used to nucleate a'-SiAlON grains in the ceramic to allow tailored grain growth. We have developed a theory for grain growth, based on the recent observations of the morphology of isolated grains from the oxynitride liquid. This model successfully predicted the novel shape transition observed experimentally. We have developed a theory to describe the chemical potential of anisotropic grains under equilibrium and non-equilibrium conditions. This model is applicable for both silicon nitride and silicon carbide. We have developed a wet chemical technique for etching the highly stable a'-SiAlON, which until now has proved difficult for ceramographic preparation. We have shown that the mechanical strength of a'-SiAlON can exceed 1 GPa and the strength retention is good at least up to 1350oC.			
14. SUBJECT TERMS		15. NUMBER OF PAGES 5	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT U	18. SECURITY CLASSIFICATION OF THIS PAGE U	19. SECURITY CLASSIFICATION OF ABSTRACT U	20. LIMITATION OF ABSTRACT

I. TITLE OF PROJECT

IN-SITU TOUGHENED α' -SIALON

PROGRESS REPORT
August 16, 1999-AUGUST 31, 1999
&
FINAL REPORT
NOVEMBER 15, 1997-November 15, 2000

U.S. AIR FORCE GRANT NO. F49620-98-1-0126

PRINCIPAL INVESTIGATOR

I-WEI CHEN

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA

II. OBJECTIVES

Basic research on the physical chemistry, processing, and mechanical properties of α' -SiAlON is conducted to capitalize on the recent discovery of this family of silicon nitride solid solution that can be self reinforced by elongated, interlocking grains. Compared with conventional β -Si₃N₄, these new materials have the advantage of higher hardness; in addition, they have broader compositional freedom that could be advantageous for tailoring chemical and physical compatibility in system applications. The core research will delineate the basic phase relations and phase boundaries for the family of rare-earth (R)-stabilized α' -SiAlON (R=Nd, Sm, Gd, Dy, Yb, and Y), determine the optimal compositions for favorable sinterability and long term stability, establish the methodology of heat treatment for developing grain-interlocking microstructure, and compare the kinetics of phase transformation and abnormal/anisotropic grain growth. This is done by using starting powders of different compositions and under high temperatures including both static and deformation conditions. Comprehensive mechanical characterization will also be conducted to investigate the strength/hardness-temperature relationship, toughness-temperature microstructure relationship, and creep-phase-transformation relationship. This will be further complemented by a modeling effort to understand the thermomechanical behavior of these new ceramic alloys.

III. STATUS OF EFFORT

The grant was initiated on November 15, 1997. We have explored the compositions at which in-situ toughened α' -SiAlON can be obtained. This essentially encompasses the entire single α' -phase region. It includes both rare-earth ion-added compositions and alkali-earth ion-added compositions. We have made a systematic effort to obtain kinetic data on phase transformation at different compositions, since this knowledge is critically important for the precise control of nucleation and growth which dictate the microstructure. We have developed methods for controlling microstructure in α' -SiAlON prepared from commercial α -Si₃N₄ powders. These materials have faster transformation rate and the microstructure control must rely on nucleation treatment of external seeding. We have developed the method to grow and harvest seed crystals, of a controlled composition, size and morphology, which can be used to nucleate α' -SiAlON grains in the ceramic to allow tailored grain growth. We have developed a theory for grain growth, based on the recent observations of the morphology of isolated grains from the oxynitride liquid. This model successfully predicted the novel shape transition observed experimentally. We have developed a theory to describe the chemical potential of anisotropic grains under equilibrium and non-equilibrium conditions. This model is applicable for both silicon nitride and silicon carbide. We have developed a wet chemical technique for etching the highly stable α' -SiAlON, which until now has proved difficult for ceramographic preparation. We have shown that the mechanical strength of α' -SiAlON can exceed 1 GPa and the strength retention is good at least up to 1350°C. We have obtained R-curves for α' -SiAlON ceramics, and show that they can reach a toughness of 11-12 MPa m^{1/2}, which compares favorably with the state-of-the-art β silicon nitride.

IV. ACCOMPLISHMENTS/NEW FINDINGS

Nucleation Control of Microstructure

The essence of microstructure control that enables the formation of in-situ toughened α' -SiAlON is to control nucleation of α' phase so that relatively few nuclei compete for growth. There are three general ways to achieve this goal. First, starting powders can be chosen to be energetically more stable or crystallographically less similar to the product phase. This implies that β - Si_3N_4 powders are better as the starting powders. The second method is to choose a composition with less stability for the α' phase. This dictates the choice of larger cations or compositions near the phase boundary. An extension of the second approach is to take advantage the temperature dependence of the phase stability. This dictates the use of lower temperature for nucleation. We have demonstrated that these three approaches, individually or in combination, with various conceivable variations, can be practiced to render any single phase α' -SiAlON composition amenable to obtaining a fibrous microstructure.

We have found that for highly stable single phase α' -SiAlON compositions the above approaches can not be practiced because the driving force is too large and nucleation rate too fast. In such a case, we have introduced seed crystals of single phase α' -SiAlON composition to predetermine the nucleation statistics. This approach has proved successful. As a result, we are now able to obtain high toughness single phase α' -SiAlON ceramics of any composition using either α or β - Si_3N_4 powders.

A parallel effort has been made to prepare α' -SiAlON seeds of an appropriate size and shape. It is noted that, to be effective, seeds must have the same composition of the final phase, or have a composition that is thermodynamically more stable. This is a difficult task compared with the other seeding efforts reported in the literature, where the seeding can be provided simply by using compounds of an appropriate phase, e.g. β - Si_3N_4 or α SiC. In our case, such compounds invariably dissolve, so the seeds need to have a composition that is stable, i.e., it should be an α - Si_3N_4 solid solution itself. This task has been succeeded and a method for obtaining high-yield seed crystals of a variety size, shape and compositions have been developed. The physical chemistry of seed formation and growth has been investigated.

Our research on α' -SiAlON has also systematically explored the difference between compositions involving (a) rare earth cations of different sizes and (b) alkali earth cations, primarily Ca. The stability of the single phase α' -SiAlON varies significantly and this has a major impact on the phase nucleation and microstructural development of the ceramics. In addition, the kinetics are influenced by the different liquid viscosity due to the presence of different cations. By controlling these factors separately, it is now possible to obtain the desired microstructure for all the rare-earth cation α' -SiAlON and for Ca- α' -SiAlON.

Mechanical Properties of α -SiAlON

We have investigated the mechanical properties of α -SiAlON using three methods. Preliminary hardness and toughness data were obtained using the indentation method. Although toughness is usually underestimated by this method, the systematic

trend between ceramics of different compositions and different microstructures is usually preserved. A more systematic investigation has been made using R-curve measurements. This was performed in-situ under a microscope in the four-point bending configuration. The R-curves show a very strong correlation with the microstructure and are sensitive to the compositions. The values at small crack extension, approximately 50-100 μm , appear to correspond well to the values of indentation toughness. Very high toughness of 11-12 $\text{MPa m}^{1/2}$ is seen in some microstructures, which compares favorably with the toughness of in-situ toughened β -silicon nitride. Finally, three-point bending has been performed to obtain strength data at room temperature and elevated temperatures, up to 1350 $^{\circ}\text{C}$. Strength values exceeding 1 GPa have been obtained in some ceramics, which can be retained (up to 70%) at high temperatures. Further optimization of the strength-toughness combination seems possible but has not been performed.

Thermodynamics of Anisotropic Si_3N_4 Crystals

The recent observation of Wang, Tien and Chen on β - Si_3N_4 showed that an elongated rod grown from the liquid can have a concave end. Such morphology implies that material transport must come from the corner, and it in turns implies long range surface diffusion along the side surface. Interface control is obviously an important factor in directing growth anisotropy. We have developed a thermodynamic theory for the chemical potential of surface atoms of an anisotropic crystal, with and without facet, under equilibrium and non-equilibrium conditions. The equilibrium shape has been obtained, and criterion for shape evolution has also been formulated. Using this theory, the evolution of the aspect ratio of grains during phase transformation and Oswald ripening can now be understood. In addition, the case of interface control can also be rigorously treated with respect to the underlying equilibrium conditions to account for different growth scenarios. This theory has been extended to silicon carbide as well. Experimental effort to determine the shape evolution of several anisotropic growth systems is in progress.

Microstructure Determination of α' -SiAlON

We have developed a new chemical etching technique that reveals the microstructure clearly under a light microscope. The new technique takes advantage of the bonding difference between nitride and oxide to differentially dissociate the Si-O-Si bond and the Si-N-Si bond. Alternatively, the nitrogen bond can be converted to oxygen bond resulting in a large change in refractive index. This technique makes it feasible to perform quantitative microscopy using image analysis softwares.

A new development in quantifying the microstructure of anisotropic grains has been made. Such microstructure must rely upon information on two-dimensional cross sections. Previous methods measured rectangular shapes on such cross sections; the statistics of such shapes are compared, using reverse transformation, with postulated three-dimensional shape statistics. We have shown that a linear intercept method works equally well for self-similar shapes. The advantage to the linear intercept method is that it is much faster for data collection, and it has much better sampling statistics.

V. PERSONNEL SUPPORTED

I-Wei Chen (Principal Investigator)
Joosun Kim (Post-Doc)
Roman Shuba (PhD student)
Misha Zenotch (Visiting research student)

VI. PUBLICATIONS

- (a) I-Wei Chen and A. Rosenflanz, "A Tough SiAlON Ceramic Based on alpha Si_3N_4 with a Whisker-like Microstructure," *Nature*, 389, 701-04 (1997).
- (b) L-L. Wang, T-Y- Tien, and I-Wei Chen, "Morphology of Silicon Nitride Grown from a Liquid Phase," *J. Amer. Ceram. Soc.* 81 [10] 2677-86 (1998).
- (c) I-Wei Chen, "Modeling Challenges in Ceramic Materials Innovation," *Current Opinion in Solid State & Materials Science*, 3, 538-43 (1998).
- (d) A. Rosenflanz and I-Wei Chen, "Phase Relationships and Stability of α' -SiAlON," *J. Amer. Ceram. Soc.* 82 [4] 1025-36 (1999).
- (e) I-Wei Chen and M. Engineer, "Model for Fatigue Crack Growth in Grain-Bridging Ceramics," *J. Am. Ceram. Soc.*, 82 [12] 3549-60 (1999).
- (f) A. Rosenflanz and I-Wei Chen, "Kinetics of Phase Transformations in SiAlON Ceramics I. Effects of Cation Size, Composition and Temperature," *J. Europ. Ceram. Soc.*, 19, 2325-35 (1999).
- (g) A. Rosenflanz and I-Wei Chen, "Kinetics of Phase Transformations in SiAlON Ceramics II. Reaction Paths," *J. Europ. Ceram. Soc.*, 19, 2337-48 (1999).
- (h) J-S. Kim and I-Wei Chen, "Microstructure Control of In-Situ Toughened α -SiAlON Ceramics," *J. Amer. Ceram. Soc.*, 83 [7] 1819-21 (2000).
- (i) L-L. Wang, T-Y. Tien, and I-Wei Chen, "Reply to Comment on "Morphology of Silicon Nitride Grown from a Liquid Phase," *J. Amer. Ceram. Soc.*, 83 [3] 677-78 (2000).
- (j) M. Zenotchkine, R. Shuba, J-S. Kim and I-Wei Chen, "R-Curve Behavior of In-situ Toughened α -SiAlON Ceramics," *J. Am. Ceram. Soc.*, accepted (2000).